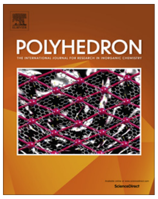
Polyhedron 116 (2016) 105–110

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Bis(phenolato)molybdenum complexes as catalyst precursors for the deoxydehydration of biomass-derived polyols

Klaus Beckerle, Andreas Sauer, Thomas P. Spaniol, Jun Okuda [*]

Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, 52056 Aachen, Germany

ARTICLE INFO

Article history:
Received 28 January 2016
Accepted 25 March 2016
Available online 6 April 2016

Keywords:
Deoxydehydration
Molybdenum bis(phenolate) complexes
Biomass conversion
Catalysis
Polyols

ABSTRACT

Bio-based polyols can be converted to olefins and furan derivatives in one step by combined reduction and dehydration (deoxydehydration, DODH). A series of octahedral complexes of hexavalent molybdenum containing an (OSSO)-type bis(phenolate) ligand were prepared and structurally characterized. These complexes were screened as catalyst precursors for the deoxydehydration of anhydroerythritol using 3-octanol as reducing agent. Microwave heating allows a lower reaction temperature.

1. Introduction

Transformation of biomass into platform chemicals and fuel components requires efficient methods to reduce the oxygen content [1]. Especially the abundant cellulose and hemicellulose fractions that are made up from sugar molecules contain a high oxygen to carbon ratio. Hydrogenation of cellulosic materials has been intensely studied, but sustainable sources for dihydrogen are still limited. Alternative pathways include deoxydehydration (DODH) that formally combines dehydration with reduction in one step. This procedure could transform C_6-sugar alcohols directly to furan derivatives or to oxygen-free unsaturated hydrocarbons.

Until now, the most efficient catalysts for deoxydehydration such as $[CH_3ReO_3]$ (methyltrioxorhenium, MTO) contain rhenium [2]. This rare and expensive metal should be avoided if DODH is performed economically on a large scale. A solution may be found with more abundant metals such as molybdenum or vanadium which show properties related to rhenium. Deoxydehydration catalysts based on either of these metals have already been reported but are generally not as efficient as rhenium-based systems [2c,3].

High-valent molybdenum compounds supported by phenolate ligands are known to catalyze oxygen transfer reactions and may be considered as models for oxotransferases [4]. These compounds are usually based on salen- or salan-type ligands, but sulfur bridged bis(phenolate)s were also studied [5]. We have now extended our work on bis(phenolate) metal complexes to the coordination chemistry of Mo(VI) compounds and their reactivity in deoxydehydration catalysis (see Scheme 1).

2. Results and discussion

2.1. Synthesis and characterization

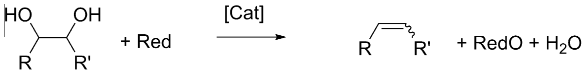
Among the bis(phenolate) ligands, the tetradentate dianionic (OSSO)-type ligand framework is especially versatile since several parameters allow to adjust the properties of a molecular catalyst. Substituents in *ortho*-position are shielding the metal center and influence the electron density. The length of the linker between the two phenol moieties determines the molecular fluxionality. We synthesized a range of molybdenum complexes bearing these tetradentate ligands before testing them in DODH reactions. The SCH_2CH_2S bridge in proligands **1a–c** previously gave rigid complexes of group 4 metals, provided the *ortho*-substituent is larger than isopropyl [6]. The related C_3-bridge in ligand **2** is known to give less rigid complexes [7]. Substituents in *ortho*- or *para*-position of the aromatic ring were also varied. All metal complexes (**3a–c**, **4**) were prepared via a straightforward route by eliminating HCl using triethylamine (Scheme 2) [8].

The behavior of the complexes in solution was studied by NMR spectroscopy. Complex **3b** with *tert*-butyl substituents in *ortho*- as well as in *para*-position shows two sharp doublets for the four protons of the 1,2-ethanediyl bridge; two singlets are found for the four *tert*-butyl groups (Fig. 1). Non-fluxional coordination at 23 °C is clearly indicated. The related molybdenum complexes **3a** and **3c** only vary by their smaller substituents at the aromatic ring

---

[*] Corresponding author.
E-mail address: jun.okuda@ac.rwth-aachen.de (J. Okuda).

http://dx.doi.org/10.1016/j.poly.2016.03.053
0277-5387/© 2016 Elsevier Ltd. All rights reserved.

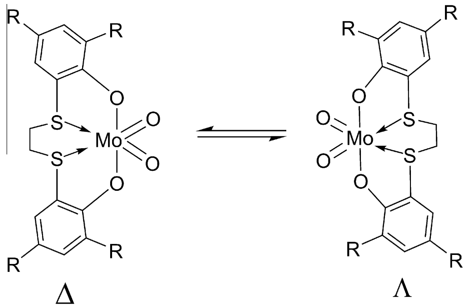


Scheme 1. Catalytic deoxydehydration (DODH).

(H or Cl instead of the *tert*-butyl groups). These are fluxional with coalescence temperatures around 23 °C, as shown by the resonances of the protons of the CH_2CH_2 bridge that appear as broad signals due to interconverting helical structures (Scheme 3) [9].

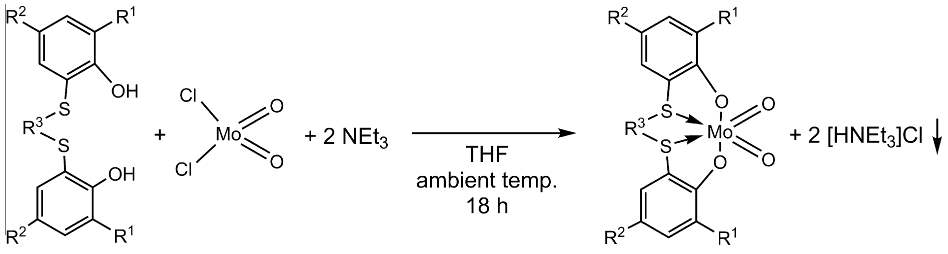
The ^1H NMR spectrum of **3a** (R^1, R^2 = H) at 23 °C shows a pair of broad signals just below coalescence, typical for a slow exchange process within a CH_2CH_2 fragment (Fig. 1). In the dichloro substituted compound **3c**, a very broad signal between 2.5 and 3.8 ppm at 23 °C indicates coalescence and thereby an enhanced exchange rate at this temperature; this signal sharpens upon heating. The ^1H NMR spectrum of **4** at 23 °C shows two multiplets due to the $A_2A'_2XX'$ spin system [6,7]. This agrees with a fluxional C_3 bridge. Below −37 °C, the spectral pattern of **4** indicates that the exchange process is frozen (Fig. 2).

The signal of the central $CH_2CH_2CH_2$ protons remains broad down to −77 °C. Within the temperature range studied (−77 to +23 °C), the two signals of the *tert*-butyl groups remain distinct showing that the C_2-symmetrical trans-O,O configuration is maintained (Scheme 4b).



Scheme 3. Interconverting Δ- and Λ-helical species in the C_2-bridged complexes.

The analogous (ONNO)-complex **6** was synthesized to examine the influence of a bridge with harder N donors that due to the stereogeneity of the amine donors can be expected to be more stereorigid (Scheme 5). ^1H NMR spectroscopic analysis shows two singlets for the *tert*-butyl groups confirming C_2-symmetry. The ethylene bridge is observed as a multiplet in THF-d_8, while a typical AA′BB′-pattern appears in CD_2Cl_2.



1a	R^1, R^2 = H; R^3 = $-CH_2CH_2-$	**3a**
1b	R^1, R^2 = ^{t}Bu; R^3 = $-CH_2CH_2-$	**3b**
1c	R^1, R^2 = Cl; R^3 = $-CH_2CH_2-$	**3c**
2	R^1, R^2 = ^{t}Bu; R^3 = $-CH_2CH_2CH_2-$	**4**

Scheme 2. Synthesis of the molybdenum(VI) complexes **3a–c** and **4** with an (OSSO)-type ligand.

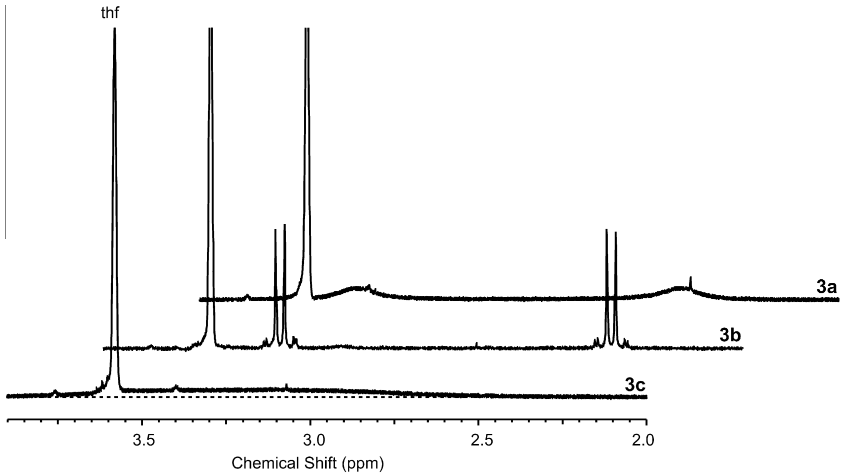


Fig. 1. ^1H NMR spectroscopic signals of the protons of the SCH_2CH_2S bridge in **3a–c** (23 °C, THF-D_8, the dashed line represents the expected baseline).